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Applicant: Yuichi TSUJI, et al.

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Title: THERMOCONDUCTIVE ADDITION-CURABLE LIQUID SILICONE RUBBER
COMPOSITION AND COATED FIXING ROLL

DECLARATION UNDER 37 CFR § 1.132

**Mail Stop: Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450**

Dear Sir:

I, Hiroaki Yoshida, hereby state that:

1. I am a citizen of Japan.
2. I have a Master of Engineering degree in polymer science from Tokyo University of Agriculture and Technology. I am currently employed in a rubber technology specialist role for Dow Corning Toray Silicone Co., Ltd. of Tokyo, Japan. I have worked in the silicone field for 16 years and I have been employed by Dow Corning Toray for the past 16 years.

3. I am a named inventor of the pending U.S. Patent Application, Serial No. 10/553,274, and a person highly skilled in the siloxane art, including siloxane polymers, components thereof, processes for producing siloxane polymers, and compositions including siloxane polymers.

4. I am aware of, have read, and understand the disclosure of U.S. Pat. No. 4,515,884 to Field et al. (Field), which is entitled "FUSING SYSTEM WITH UNBLENDED SILICONE OIL", and has an equivalent family member of JP59069773 (A).

5. I am aware of, have read, and understand the disclosure of U.S. Pat. No. 5,869,188 to Priebe et al. (Priebe), which is entitled "ELECTROSTATOGRAPHIC MEMBER AND SYSTEM FOR ELECTROSTATOGRAPHIC REPRODUCTION AND METHOD FOR PREPARING THE SAME".

6. I am aware of, have read, and understand the disclosure of U.S. Pat. Appl. Publ. No. 2002/0146575 to Shudo et al. (Shudo), which is entitled "LIQUID FORM ADDITION CURING TYPE SILICONE RUBBER COMPOSITION FOR FLUORORESIN COVERED FIXING ROLLER AND FLUORORESIN COVERED FIXING ROLLER" , and has an equivalent family member of JP2002302607 (A).

7. For the reasons described in Paragraphs 8 through 18 immediately below, our invention is unique and distinguishable from the teachings of Field, Priebe, and Shudo, either alone, or in combination

8. Referring to the teachings of Field, Field is directed toward a fusing system including a fusing surface formed by a silicone rubber. Although Field initially introduces silicone rubbers and describes various *vulcanization* methods of the silicone rubbers, e.g. RTV, LTV, etc., these methods do not convey a particular *cure* mechanism for the silicone rubbers, e.g. a condensation-cure mechanism. However, Field later teaches that its silicone rubbers are formed from a coating composition cured by condensation-cure. The cure mechanism of Field is gathered from teachings related to the crosslinking catalyst of the coating composition, which is preferably tin-based (column 11, lines 21-46 of Field). One skilled in the art readily recognizes that such tin-based catalysts are indicative of condensation-cure systems. Conversely, addition-cure systems can readily be determined based on the presence of a platinum-based catalyst.

9. Based on my extensive work with various cure systems, it has been my experience that condensation-curable silicone materials, especially those employing a tin-based catalyst, have lower heat resistance relative to addition-curable silicone materials. Part of this heat resistance issue is related to the fact that condensation-cure reactions are reversible, especially at higher temperatures, e.g. 80 °C or higher. Referring to page 582 of Appendix A attached herewith, it is taught that reversion occurs due to the presence of residual alcohol and tin-based catalyst within the cured silicone. As such, as temperature rises, residual alcohol is released, the cured silicone reverts, and cured silicone loses physical integrity.

10. In our invention, our silicone rubber layer, which is formed via an addition-cure mechanism, is typically coated with a fluororesin or fluororubber layer during end application in a fixing roll. If we were to use a condensation-cure system like that of Field, the reversion issue described above would only be worse. This is because as temperature rises, the released alcohol would not be able to escape, due to physical confinement by the fluororesin or fluororubber layer. As such, the alcohol would freely interact with the tin-based catalyst and the condensation-cured silicone rubber would degrade, as described above and in Appendix A.

11. Further, relative to the end applications of Field, our silicone rubber layers are generally exposed to higher temperatures, such that higher heat-stability and adhesion stability is required. For example, in column 12, line 27 of Field, it is taught that its coated fuser roll is exposed to a maximum temperature of 385 °F. This temperature is much lower than a typical end application of our silicone rubber layer, which can be 230 °C/446 °F or more, as described in our Examples.

12. For the reasons set forth in Paragraphs 8 through 11 above, it is clear that silicone rubber compositions based on condensation-cure systems and addition-cure systems are not equivalent, in both the chemical *and* physical sense. Specifically, as described above, each type of silicone rubber is based on a reaction involving a different type of catalyst. In addition, condensation-cured systems suffer from reversion issues at higher temperatures, whereas addition-cured systems generally do not. This is not to say

that condensation-cured systems do not have any advantages over addition-cured systems, but such advantages are evaluated based on applications of the particular system. For example, curing of addition-cured systems can be impaired by various substances, e.g. sulfur compounds, whereas condensation-cured systems are typically only impaired by lack of water.

13. Referring to the teachings of Priebe and Shudo, both of these references focus on addition-cure systems. As described above, because addition-cure systems are not equivalent to condensation-cure systems, one skilled in the art, such as myself, would not have turned to the teachings of Field in view of Priebe and/or Shudo, or vice-versa, at the time of our invention. This is especially true based on the clear disadvantages of condensation-cure systems when exposed to higher temperatures, such that one attempting to formulate a silicone rubber composition for higher temperature applications would only look to addition-cure systems, not condensation-cure systems.

14. In addition, because the silicone rubbers of Field are limited to lower temperature end applications as described above, one skilled in the art would not turn to the teachings of Field when attempting to address issues in higher temperature end applications. If anything, one skilled in the art would have likely dismissed the teachings of Field altogether as being “antiquated” technology when attempting to address issues in higher temperature end applications.

15. For the reasons described in Paragraphs 9 through 14 above, one skilled in the art, prior to our invention, would not have combined the teachings of Field with the teachings of Priebe and/or Shudo or vice-versa. In addition, even if one were to combine the teachings of Field with the teachings of Priebe and/or Shudo, the results would not have been predictable as described in Paragraphs 16 and 17 immediately below.

16. First, I submit herewith Tables 5 and 6 of our application with quantitative values for the cohesive failure ratio. In addition, referring to Tables 1a and 1b of our application, I note that we generally ran our testing of the compositions on an equal loading comparison, to minimize as many variables as possible, rather than on a normalized loading comparison. For example, the only loading difference between Example 1 and Comp. Ex. 3 is the presence or lack of component (D), respectively. If we were to have normalized Comp. Ex. 3 to make up for the lack of component (D), it would have been unclear which component or components imparted or subtracted the physical properties we sought to improve, e.g. adhesion strength.

Table 5:

Examples	Adherence to aluminum panel (cohesive failure ratio)				
	initial	after 170 hours	after 220 hours	after 310 hours	after 480 hours
Example 1	100	100	100	100	100
Example 2	100	100	100	100	100
Example 3	100	100	100	100	100
Example 4	100	100	100	100	100
Example 5	100	100	100	100	100
Comp. Ex. 1	100	77	83	66	73
Comp. Ex. 2	82	75	63	42	33
Comp. Ex. 3	87	95	82	75	65
Comp. Ex. 4	75	73	63	35	20
Comp. Ex. 5	80	75	58	35	15
Comp. Ex. 6	88	93	65	43	33

Table 6:

Examples	Adherence to fluororesin (cohesive failure ratio)				
	initial	after 170 hours	after 220 hours	after 310 hours	after 480 hours
Example 1	100	100	100	100	100
Example 2	100	100	100	100	100
Example 3	100	100	100	100	100
Example 4	100	100	100	100	100
Example 5	100	100	100	100	100
Comp. Ex. 1	100	75	60	38	15
Comp. Ex. 2	83	65	40	25	0
Comp. Ex. 3	100	100	100	85	75
Comp. Ex. 4	85	40	15	0	0
Comp. Ex. 5	10	20	55	60	0
Comp. Ex. 6	75	100	40	15	0

17. Surprisingly, in our invention, I, along with my co-inventor, discovered that with a specific combination of components, we were able to form silicone rubber layers with excellent physical properties, especially increased adherence to various substrates over time during high temperature end applications. For example, as illustrated above, all of our inventive Examples 1-5 maintain adherence even after 480 hours at high temperature. Conversely, none of the Comparative Examples have such results. The specific combination of components in our invention presents a synergistic effect with regard to this adhesion strength, and not just an additive effect, based on the types and amounts of micropowders we evaluated during our discovery.

18. **Conclusions**

For the reasons described in Paragraphs 9 through 17 above, our invention is unique and distinguishable from the teachings of Field, Priebe, and Shudo. Specifically, none of these references would direct one skilled in the art to evaluate the teachings of the other(s). In addition, I, along with my co-inventor, first discovered that a specific combination of micropowders imparts excellent adhesion strength properties to addition-cured silicone rubbers, such that our invention presents new and unexpected results relative to the prior art, including Field, Priebe, and Shudo.

19. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information are believed to be true, and further that these statements were made with the knowledge that willful and false statements and the like are

punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or patent issued thereon.

Respectfully submitted,

Dated 28. October, 2010

Hiroaki Yoshida

Hiroaki Yoshida

Siloxane Polymers

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APPENDIX A

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It can be concluded therefore that the peroxide-induced free radical cross-linking of polydimethylsiloxanes is capable of producing different cross-linked matrices depending on the choice of peroxide and polymer. An unmodified polydimethylsiloxane can only be cured by using significant levels of aryloxy peroxide and this system will produce a randomly cross-linked matrix with the cross-link being a two-carbon ethylene bridge. A vinyl-modified polydimethylsiloxane can be successfully cross-linked with a wider choice of peroxides. Using an aryloxy peroxide (at a much lower level than for unmodified polydimethylsiloxane) will yield a randomly cross-linked matrix, the number and position of the cross-links not being controlled by the vinyl group concentration or position. The chemical nature of the cross-link is a mixture of two-, three- and four-carbon bridges with the two- and three-carbon bridge type predominating. Using vinyl-specific peroxides, such as dialkyl peroxides, the cross-linked matrix produced is controlled to a significant extent by the number and position of the vinyl groups. The cross-links formed are once again a mixture of two-, three- and four-carbon bridges but in this case three- and four-carbon bridges predominate.

The influence of the quantity and position of vinyl groups in the polydimethylsiloxane on the nature of the cross-linked matrix produced using vinyl-specific peroxides would suggest that polymer design could be a significant variable in controlling the final properties of the silicone rubber. However, in practice, the most convenient method of making polydimethylsiloxane gums containing vinyl groups is the base catalyzed equilibrium copolymerisation of dimethyl cyclosiloxanes and methylvinyl cyclosiloxanes, which the work of Saam and Ziemelis (16) has shown, produces a polymer with randomly distributed vinyl groups. The convenience of this process and the fact that it is essential to add fillers, such as silica, to the cross-linked polydimethylsiloxane matrix to produce acceptable commercial rubber has meant that the development of more complex manufacturing process to produce other vinyl group distribution has not been encouraged. In fact, because of the marked effect of addition of fillers on the final material properties most of the product development effort has been focused on filler choice and treatment, at the expense of a more extensive study of the effect of polymer architecture.

In order to establish control over the properties of the silicone rubber the silicone rubber technologist has had to resort to an extensive empirical evaluation procedure involving formulating and physically testing rubbers with different gums, peroxides, and fillers. These studies have resulted in an excellent portfolio of rubber products and well-documented formulations (8, 12, 17). It has also been discovered that postcuring, that is a further heating cycle following the heat cycle used to initiate the cross-linking reaction, greatly enhances the final properties and performance of the compounded rubber. It is now generally accepted that postcuring removes

the volatile byproducts from the cross-linking step and generally stabilizes and improves properties such as compression set and heat stability of the final rubber.

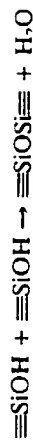
In spite of much research and development, covering a whole range of peroxides, no one peroxide has yet been identified which will satisfy all the various industry requirements.

The silicone rubber technologist, therefore, employs a range of siloxane polymers and a limited range of peroxides, typically, 2,4 dichlorobenzoyl peroxide, dicumyl peroxide and di-*t*-butyl peroxide to achieve the required rubber properties. Thus, 2,4 dichlorobenzoyl peroxide is used for hot air vulcanization, dicumyl or di-*t*-butyl peroxide are used with vinyl-containing siloxane polymers for thick section cured materials or for carbon black containing silicone rubber stocks. As a general statement, vinyl specific peroxide cross-linked rubbers need less postcure and have a lower compression set than those cross-linked with nonvinyl specific peroxide.

The results of this adaptation of science and technology are silicone rubbers that have uses in a wide range of applications where good temperature stability, electrical insulation, and chemical stability are important.

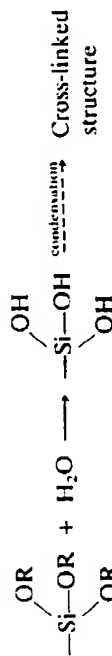
12.3 CROSS-LINKING USING CONDENSATION REACTIONS

The condensation of silanol groups to form siloxane bonds

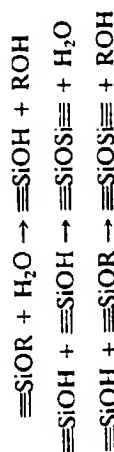


is a reaction of considerable importance in industrial silicone chemistry. If it were feasible to extend this chemistry to molecules where more than one silanol group is attached to a single silicon atom, then this condensation reaction could be used to produce a three-dimensional cross-linked matrix with the desirable absence of any additional organic character, since the cross-links would be siloxane bonds. However such silanols readily undergo spontaneous condensation and therefore cannot be used *per se* for cross-linking polydimethylsiloxane polymers. The principle, however, has been harnessed successfully in so-called room temperature curing systems. It is known that many groups attached to silicon are readily hydrolyzed to produce silanol groups. In particular alkoxy, acyloxy and oxime ($-\text{OR}$) groups are known to undergo this reaction. Furthermore, in the absence of moisture, these groups do not react even when there is more than one $-\text{OR}$ group attached to a single silicon atom. Therefore, in room temperature curing systems, molecules are synthesized which contain $\equiv\text{Si}(\text{OR})_2$ or $-\text{Si}(\text{OR})_3$ groups as part of the siloxane chain and these

groups, on exposure to atmospheric moisture, spontaneously hydrolyze and condense to give a three-dimensional cross-linked network.



If we include the initial hydrolysis of the —OR functional group attached to silicon then there are three possible reactions involved in the cross-linking process.



In practice the systems used are derived from the reaction of α,ω silanol-terminated polydimethylsiloxanes with tetra or trifunctional silanes under controlled conditions. The product of this reaction is a trifunctional- or difunctional-terminated polydimethylsiloxane which, on exposure to moisture yields the cross-linked matrix.



It is immediately clear that this chemistry can be adapted to give a one-pack or two-pack product depending on when the silanol and the silane are mixed. If the materials are mixed immediately prior to use then this constitutes a two-pack system. If they are mixed and stored prior to use then we have a one-pack system. In this latter case it is essential that the material is protected from moisture.

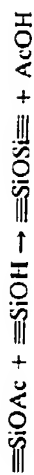
12.3.1 Acetoxy-Functional Condensation Systems

One of the earliest room temperature curing systems involved the use of acetoxy functional silanes (18, 19), which because of the extreme reactivity of these silanes, was used as a one-pack system. An α,ω silanol polydimethylsiloxane was reacted with excess triacetoxy silane either $\text{MeSi}(\text{OAc})_3$, or $\text{EtSi}(\text{OAc})_3$. Cross-linking was effected by exposing the reaction product, which is nominally a diacetoxy end-blocked polymer, to atmospheric moisture. This results in cleavage of the acetoxy group to produce a silanol group and acetic acid.



Cross-Linking Using Condensation Reactions

Cross-linking occurs by reaction of the silanol group with another acetoxy group:



or with another silanol group:



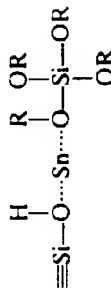
to produce a three-dimensional network. Mallam, Hecht and Geissler (20) have studied the structure of a typical acetoxy silane cross-linked unfilled polymer matrix using light-scattering and neutron-scattering techniques. They used an α,ω silanol polydimethylsiloxane of viscosity 20 Poise and ethyltriacetoxy silane $[\text{EtSi}(\text{OAc})_3]$ as the cross-linking agent. The resulting gels were swollen in octane and examined by light-scattering and neutron-scattering techniques. The study revealed that the swollen matrix of cross-linked polydimethylsiloxane contained particles of 800 Å average radius, arising from the hydrolysis of the excess ethyltriacetoxy silane, some of which exist as visibly large aggregates, the rest being distributed throughout the network as lower molecular weight species. A closer examination of the swollen polydimethylsiloxane suggests that there is an uneven distribution of cross-links.

The rate at which cross-links are formed (rate of cure) is controlled by the rate of diffusion of water and, therefore, by the relative humidity in the environment. The thickness of the section that can be cross-linked is dictated by the rate of diffusion of moisture into the section. It is probable that as cross-linking proceeds the rate of diffusion of water will decrease since it has to diffuse through a cross-linked matrix. This constraint is common to all room temperature curing systems based on condensation reactions. The major limitation to the use of this acetoxy-based cure system is the liberation of the corrosive acetic acid which, aside from its unpleasant odor, has significant detrimental effects on many substrates. However, in spite of this limitation, the acetoxy system has been developed into a very successful range of products most notably for use as domestic caulks where its excellent adhesion to ceramic surfaces has been a significant benefit.

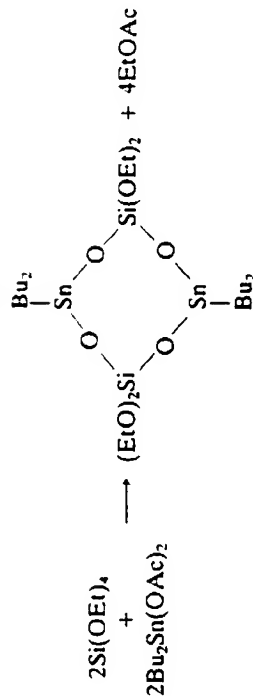
12.3.2 Alkoxy-Functional Condensation Systems

The need for a system that does not liberate acetic acid has encouraged the search for alternative hydrolyzable groups. The most versatile has proved to be the silicon-alkoxy group, especially $\equiv\text{SiOMe}$ and $\equiv\text{SiOEt}$ (21, 22). Because this system is slower reacting than the acetoxy system it requires the addition of a catalyst to achieve acceptable rates of cross-linking. This is slower, and therefore more controllable, reaction rate means that the system can be formulated as a one- or a two-pack system.

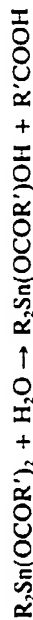
Two-Pack System. The two-pack system typically uses tin carboxylates as catalysts, although other metal carboxylates such as lead or cobalt can be used. The two packs are made up of separate components, one containing the α,ω silanol polydimethylsiloxane and the other, the cross-linker plus tin catalyst. The cross-linker plus tin catalyst is often diluted in a nonreactive silicone polymer to ease the eventual mixing process. Mixing of the two components starts the cross-linking process. Initially it was assumed that the major cross-linking process involved reaction between the alkoxy silane and the α,ω silanol polydimethylsiloxane and that the catalytic mechanism involved the formation of a complex between the tin, the polymer and the alkoxy-silane. Baranovskaya and co-workers (23) suggested a multicenter complex, while Novikov and Nudel'man (24) following a similar line of thought, proposed a somewhat simpler form of the complex.



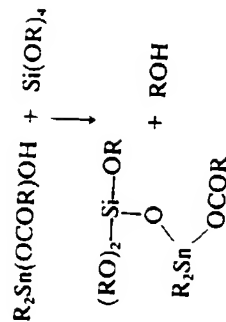
Nagy (25) invoked the formation of an organosilicon stannate



However, it is now generally accepted that the presence of atmospheric moisture plays a key role in the cross-linking mechanism. Jorg and Ernst (26) were the first to consider the role of the water, naturally present in the formulation, as being critical to the cross-linking process. They believed that the water initiated the hydrolysis of the alkoxy-silane groups to silanol groups and that the cross-linking occurred by a series of consecutive hydrolysis steps to form silanol followed by condensation of the silanol groups to give siloxane cross-links. The exact role of the tin catalyst was not defined. Further studies by Severnyi and co-workers (27) and Van der Weij (28) led to the conclusion that the role of the atmospheric moisture was to modify the tin carboxylate and convert it into an active catalytic species. Both groups of workers postulated that the first step is the partial hydrolysis of the tin carboxylate bond to produce a tin hydroxide group.

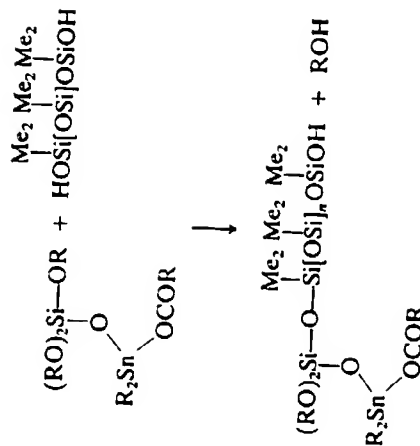


This active tin hydroxide then reacts with the silane to produce an organotin silanolate:



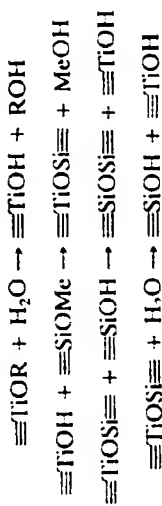
This reaction is known to occur (29) and compounds of this type have been reported as being good catalysts for the room temperature curing of siloxanes (30).

Severnnyi and Van der Weij both see the subsequent reaction of this organotin silanolate with the α,ω silanol polydimethylsiloxanes giving rise to the formation of the cross-linked network. However they differ in exactly how this reaction occurs. Severnyi sees the reaction as proceeding by silanol attack on the SiOC bond



followed by further similar reactions involving the α,ω silanol polydimethylsiloxane at the remaining SiOC bonds thus forming a cross-linked network.

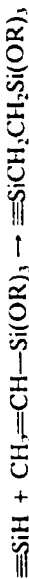
Van der Weij, however, believes that the reaction occurs via silanolysis



However, it has proved virtually impossible to identify which, if any, is the critical step and in what form the active titanate catalyst actually exists.

This one-pack technology has found application in industries where advantages can be gained from the one-pack format. Thus they are widely used in the construction industry where their good adhesion to a range of substrates and ease of application have proved of value. They have also found extensive use in the electronics industry as coatings and encapsulants where the noncorrosive nature of the alcohol byproduct of the cross-linking reaction is a distinct advantage.

An interesting extension of this technology, to increase the speed of cross-linking and produce a viable thin film coating technology, has been to introduce the alkoxyfunctionality, not by condensation, but by hydrosilylation, i.e., by addition of a carbon-carbon double bond to a silicon hydride bond.



This reaction allows the introduction of trifunctional alkoxy groups pendant to the polymer backbone as well as attached to the ends of the polymer. Such pendant siloxane systems have been shown to form films extremely quickly at room temperature. However, there is a severe drawback in terms of pot life and skin over times (a measure of surface cure) both of which are extremely short (35).

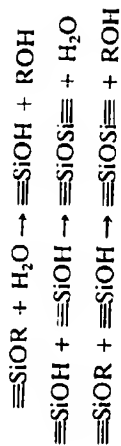
12.3.3 Oxime-Functional Condensation System

An alternative one-pack system technology has been developed based on the use of silicon oxime chemistry. The approach is similar to the one-pack alkoxy technology but, in this case, the materials used are trifunctional methylethylloximesilanes $\text{MeSi}(\text{ON}=\text{CEtMe})_3$ (36). These trifunctional silanes are reacted with α,ω silanol polydimethylsiloxanes and then stored in the absence of moisture. Exposure to moisture in the presence of a tin catalyst allows the formation of a cross-linked matrix. Once again the detailed mechanism is not understood but it is reasonable to assume that a mechanism analogous to that proposed by Severnyi and co-workers (27), and Van der Weij (28) for the alkoxy system is also applicable to this system. The attraction of the use of oxime silanes stems from the lower volatility of the liberated oxime compared to the alcohol released in the

alkoxy systems. This gives performance benefits by producing less voids due to trapped vapor, and the oxime is considered noncorrosive. This technology therefore has found application in the electronic industry where the fast surface cure and noncorrosive characteristics are beneficial.

12.3.4 Cross-Linked Matrix Formation

Although in principle the reactions that could be involved in silanol condensation cross-linking can be easily represented:



The relative importance of each reaction in the formation of the cross-linked matrix is not easily determined. The catalytic reactions of tin and titanium salts add yet another level of complexity since current thinking suggests that the role of the moisture is essential in activating the catalyst and the reaction of the $\equiv\text{SiOR}$ group with atmospheric moisture may not even be relevant to the formation of the cross-linked matrix. It should also be recognized that in the above scheme the $\equiv\text{SiOR}$ group represents a multifunctional site and it is often assumed that the reactivity of multiple $-\text{OR}$ groups on a single silicon is the same. The work of Smith (37) indicates that this is not the case. In all cases, the rates of hydrolysis for the first, second, third and fourth $-\text{OR}$ groups were different. Thus as the cross-linking reaction proceeds the reactivity of the residual $-\text{OR}$ changes. In the case of tin and titanium catalysis it is generally agreed that the reactivity decreases as the reaction proceeds and the final monofunctional $\equiv\text{SiOR}$ group is the least reactive of all.

The relative frequency of the reaction of $\equiv\text{SiOH}$ with $\equiv\text{SiOH}$ compared to $\equiv\text{SiOH}$ with $\equiv\text{SiOR}$ influences the type of cross-linked matrix formed. It is usually assumed that the critical parameter of chain length between cross-links is defined by the molecular weight of the original α,ω silanol polydimethylsiloxane used, however, if significant SiOH/SiOH condensation occurs during the cross-linking then this assumption is no longer valid. He, Widmaier, Herz and Meyer (38) have tried to resolve this issue by studying the competition between SiOH/SiOH condensation of the α,ω silanol polydimethylsiloxane and the SiOH/SiOEt reaction between the α,ω silanol polymer and trimethylethoxysilane. They used a monofunctional alkoxy silane, since this would behave as an end-blocker and limit molecular weight growth, with stannous 2-ethylhexanoate as catalyst and employed GPC and light scattering to follow the molecular weight increase. They concluded that although the end-blocking reaction predominates there is also a significant amount of silanol/silanol condensation.

This result apparently questions the usual assumption of total absence of silanol-silanol condensation in the condensation cross-linking reaction. However, it should be noted that in spite of using the least reactive form of the alkoxy-silane they concluded that the reaction of silanol with the alkoxy-silane was still the predominant reaction. In a typical cross-linking system, more reactive silanes would be employed, presumably suppressing the silanol-silanol reaction even further.

Sharaf and Mark (39) undertook a study of the chain extension reaction between α,ω silanol polydimethylsiloxane and dimethyldiethoxysilane [$\text{Me}_2\text{Si}(\text{OEt})_2$] using stannous 2-ethylhexanoate as the catalyst. They used GPC to follow the molecular weight change and verified some of the values using vapor pressure osmometry. They were able to show that the extent of reaction was greater than 90% for both polymer and the dimethyldialkoxysilane chain extender and observed some anomalous results, attributed to experimental error, when more than stoichiometric quantity of chain extender to polymer was used. They did not, however, examine the condensation of the polymer in the absence of the chain extender.

Simon, Birnstiel and Schimmel (40) have used ^1H NMR spin-spin relaxation studies to study the product of the reaction of α,ω silanol polydimethylsiloxane with tetraethoxysilane [$\text{Si}(\text{OEt})_4$]. They examined different ratios of α,ω silanol polymer: $\text{Si}(\text{OEt})_4$ and were able to show a decrease in unreacted chain ends as the level of the cross-linker increased although there was always residual unreacted chain ends even if a large excess of cross-linker was used. They also noted that the molecular weight between cross-links decreased as the level of cross-linker increased. At the stoichiometric level, however, the distance between cross-links is very close to the chain length of the polymer.

These studies, in general, support the assumptions that make the condensation cross-linking of a tetraalkoxy silane with an α,ω silanol polymer attractive as a route to model matrices which can be used to explore elastic theory. These assumptions are that the distance between cross-links is defined by the original degree of polymerization of the silanol terminated polymer; the distribution of the molecular weights between cross-links is defined by the original molecular weight distribution of the polymer; and the functionality of the cross-link is that of the original silane. There will therefore be minimum effects due to "loose end" network imperfections which are common in systems involving pendant group cure, e.g., in peroxide-induced free radical cure. A typical model system would consist of the α,ω silanol polydimethylsiloxane, a tetrafunctional silane such as tetraethoxysilane [$\text{Si}(\text{OEt})_4$] and stannous 2-ethylhexanoate as the cross-linking catalysts. The components are mixed in exact stoichiometric ratios and allowed to cross-link for 24 hours or more.

Mark and co-workers have studied an extensive series of such systems.

For single α,ω silanol polydimethylsiloxane polymers Mark and Lorente (41) observed the expected behavior. Thus the modulus depends on the molecular weight of the polymer, i.e., molecular weight between cross-links, and the modulus at rupture increases with the functionality (3 or 4) of the silane. However, when Lorente, Andradý, and Mark (42) employed mixtures of two α,ω silanol polydimethylsiloxanes, one with a low molecular weight ($M_n = 1.1 \times 10^{-3} \text{ g mol}^{-1}$) and the other of high molecular weight ($M_n = 18.5 \times 10^{-3} \text{ g mol}^{-1}$) they observed an anomalously high modulus at high extensions. They explored the use of trifunctional silane [$\text{CH}_3 = \text{CHSi}(\text{OEt})_3$] and tetrafunctional silane [$\text{Si}(\text{OEt})_4$] but found no significant differences in behavior between the two networks. Decreasing the proportion of low molecular weight α,ω silanol polydimethylsiloxane has the expected effect of decreasing the modulus, increasing elongation at break but not completely eliminating the unexpected upturn in modulus at high elongation. Using even lower molecular weight polymer ($M_n = 0.22 \times 10^{-3} \text{ g mol}^{-1}$) as diluent they (43) observed that the upturn in modulus at high elongation was much more pronounced. Mark and his co-workers have ruled out strain-induced crystallization as a possible mechanism to explain this increase in modulus and have proposed the limited extensibility of the short chains in the network as the most likely cause. They point to the gradual nature of the upturn; the reversibility observed even in the upturn portion of the stress strain isotherm; the insensitivity of the upturn to temperature and swelling; the absence of any X-ray diffraction evidence; and the absence of any birefringence even at very low temperature (-52°C); as evidence for their conclusions (44). Mark and Andradý (45) have also eliminated the possibility of reinforcement by microphase separation of the short-chain element of the matrix distribution. They performed the short-chain matrix prior to completing the cure and detected no significant change in the stress strain isotherm. These studies have shown that condensation cure has the capacity to produce a range of matrices with differing physical properties by using mixtures of high and low molecular weight α,ω silanol polydimethylsiloxanes. These matrices have very different characteristics and relationships compared to systems based on a single source α,ω silanol polydimethylsiloxane.

Mark and co-workers have extended their investigation of the model system comprising a tetrafunctional silane and α,ω silanol polydimethylsiloxane in an interesting direction. By using a large excess of the silane they have demonstrated (46) that they can obtain a reinforcing effect caused by the phase separation of the silica which is produced from the hydrolysis of the excess of the silane. While not specifically a cross-linking reaction it demonstrates the possible adaptation of silicone condensation chemistry to produce novel materials.

While all of these studies provide useful insights into the chemistry of the cross-linking reactions, and the properties of the resulting three-

dimensional matrices, the application requirements necessitate a more pragmatic approach based on choice of catalyst levels and the use of fillers to achieve the required cure characteristics and physical properties. The studies of Bajaj and co-workers (47) are typical of the data necessary to produce acceptable performance. Bajaj studied the effect of curing conditions and choice of filler and used both acetoxy and alkoxy cross-linkers. They concluded that methyltriacetoxysilane gave the quickest cure, followed by tetraethoxysilane, with methyltriethoxysilane being the slowest. Interestingly, they found that for both trifunctional silanes the molecular weight between cross-links (from swelling measurements) were very similar, but in the case of the tetrafunctional silane the molecular weight between cross-links was greater indicating a less cross-linked structure.

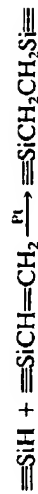
A further challenge addressed by the silicone technologist, to meet market needs, is to devise formulations which will adhere to the whole range of substrates that these cross-linked materials are applied to. Adhesion between materials can be enhanced by including polar organic groups into the system. To increase the level of adhesion of the cross-linked silicone materials it is usual to incorporate organofunctional silanes e.g., epoxy- and amine-functional silanes, into the composition. They are usually added in the form of the trifunctional alkoxy or oxime silanes so that they can participate in the cross-linking mechanism and become an integral part of the cross-linked matrix.

12.3.5 Summary

The use of the condensation reaction as a means of forming cross-linked siloxane matrices has thus been achieved by employing multifunctional silanes with hydrolyzable groups so that the desired multifunctional silanol molecules can be produced *in situ* by exposure to atmospheric moisture. In principle, any hydrolyzable group can be used but in practice acetoxy, alkoxy and oxime based systems have proved to be sufficiently versatile to meet most application requirements. The final choice of which technology is preferred is usually dictated by the specific requirements of the end applications (48, 49).

12.4 HYDROSILYLATION CROSS-LINKING

The hydrosilylation reaction, which involves the addition of a silicon hydrogen (SiH) bond to an unsaturated carbon carbon bond, catalyzed by a noble metal, typically Pt, is a well-known and versatile reaction in organosilicon chemistry. It has been widely used in the synthesis of organofunctional siloxanes and in the cross-linking of siloxane polymers. In practice the hydrosilylation reaction most frequently used is that between a hydridosilane group (SiH) and a silicon vinyl group ($\text{SiCH}=\text{CH}_2$)

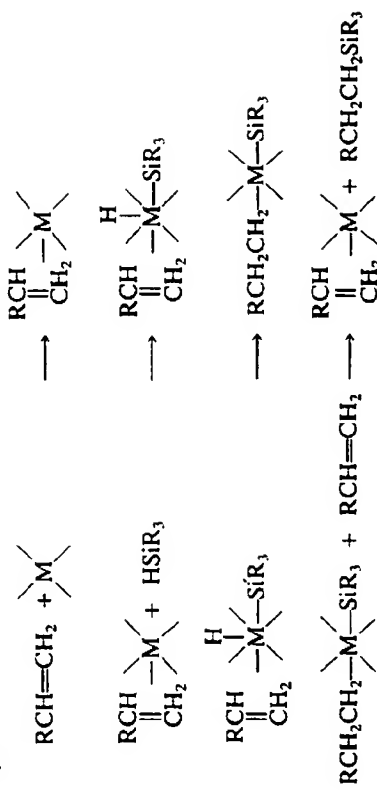


Since this reaction involves the specific interaction of $\equiv\text{SiCH}=\text{CH}_2$ and $\equiv\text{SiH}$ groups the position and number of these reactive groups effectively define the matrix that can be formed. In practice it is possible to synthesize an extensive range of polymers with the SiH and $\text{SiCH}=\text{CH}_2$ reactive groups included in a variety of positions in the polymer chain.

12.4.1 Hydrosilylation System

Following the discovery by Speier (50) that chloroplatinic acid in isopropanol would catalyze the hydrosilylation reaction many workers have investigated the mechanism of this reaction and the form of the active Pt complex. Benkeser and Kang (51) have investigated the nature of original "Speier's catalyst" (chloroplatinic acid dissolved in iso-propanol). Investigating the orange solid, collected by evaporating the catalyst solution in vacuo at room temperature, and the collected volatiles, by chemical analysis, far- and mid-infrared spectra, ^{195}Pt and ^1H nmr they concluded that the active component present was the PtII complex, $\text{H}[(\text{C}_3\text{H}_7)_3\text{PtCl}_3]$.

This complex would then catalyze the hydrosilylation process via the Chalk and Harrod (52) mechanism. This mechanism involves initial formation of a complex between the double bond of the olefinic reactant and the Pt followed by reaction with the hydridosilane and can be represented as follows



This mechanism has proved to be a useful hypothesis since it enabled workers to account for the side reactions frequently observed during hydrosilylation reactions, e.g., isomerization of the olefin, which would occur if the step involving addition of the silicon hydride is slow.

However, more recent work has revealed aspects that the Chalk and Harrod mechanism can not easily accommodate, notably the catalytic effect of oxygen on the hydrosilylation reaction. The recent investigation of the commercially preferred hydrosilylation catalyst, a complex of Pt with